THE PREDICTIVE POWER OF EXACT CONSTRAINTS AND APPROPRIATE NORMS IN DENSITY FUNCTIONAL THEORY

JOHN P. PERDEW
TEMPLE UNIVERSITY, PHILADELPHIA

CURRENT TOPICS IN THEORETICAL CHEMISTRY

QUITO, ECUADOR 2019

SOME COLLABORATORS:

JIANWEI SUN, ADRIENN RUZSINSZKY (SCAN 2015)

HAOWEI PENG, CHANDRA SHAHI, MICHAEL L. KLEIN, RICHARD REMSING, XIFAN WU, GERD CEDER, YUBO ZHANG

THIS IS A TALK ABOUT THE CONSTRUCTION PRINCIPLES FOR THE PBE GGA AND SCAN META-GGA, AND THE RESULTING PREDICTIVE POWER OF THOSE FUNCTIONALS. FOR SOME REFERENCES WITH DETAILS, PLEASE SEE THE ABSTRACT.

MANTRA OF QUANTUM CHEMISTRY:

THE RIGHT ANSWER FOR THE RIGHT REASON

MANTRA OF DENSITY FUNCTIONAL THEORY:

ALMOST THE RIGHT ANSWER FOR ALMOST THE RIGHT REASON AT ALMOST THE RIGHT PRICE FOR ALMOST ALL SYSTEMS OF INTEREST

FIRST PRINCIPLES FOR MATERIALS THEORY:

QUANTUM MECHANICS OF MANY-PARTICLE (ESPECIALLY MANY-ELECTRON) SYSTEMS

ELECTROMAGNETIC (ESPECIALLY COULOMB) INTERACTIONS

THE FIRST PRINCIPLES ARE KNOWN, BUT THEIR DIRECT APPLICATION IS STILL IMPOSSIBLE FOR ALL BUT THE SMALLEST SYSTEMS. RELIABLE "SHORT CUTS" LIKE DENSITY FUNCTIONAL THEORY OR MOLECULAR DYNAMICS ARE NEEDED.

MATERIALS: MOLECULES OR CONDENSED PHASES

COMPLEX MATERIALS: MATERIALS IN WHICH MANY DIFFERENT STATES OR PHASES COMPETE CLOSELY IN ENERGY TO BE THE GROUND OR EQUILIBRIUM STATE.

EXAMPLES:

WATER WITH ITS MANY POSSIBLE HYDROGEN-BOND NETWORKS

MATERIALS WITH PARTLY-LOCALIZED d OR f ELECTRONS, SUCH AS MANY TRANSITION-METAL OXIDES

MANY "EASILY-SWITCHED" CATALYSTS

FROM A FUNDAMENTAL POINT OF VIEW, ALL MATERIALS ARE STRONGLY-CORRELATED, AND ALL OBEY THE SAME FIRST PRINCIPLES.

THE DENSITY FUNCTIONAL THEORY OF KOHN AND SHAM, WITH THE EXACT DENSITY FUNCTIONAL FOR THE EXCHANGE-CORRELATION ENERGY, WOULD DELIVER THE EXACT GROUND-STATE ENERGY AND DENSITY OF ANY NON-RELATIVISTIC N-ELECTRON SYSTEM IN THE PRESENCE OF A MULTIPLICATIVE EXTERNAL POTENTIAL, VIA THE SELFCONSISTENT SOLUTION OF N ONE-ELECTRON SCHROEDINGER EQUATIONS (A COMPUTATIONALLY EFFICIENT ALTERNATIVE TO SOLVING THE N-ELECTRON SCHROEDINGER EQUATION).

THIS IS ALL WE NEED TO DETERMINE THE EQUILIBRIUM POSTIONS OF THE NUCLEI. WITHOUT FURTHER MODIFICATIONS, THIS THEORY DOES NOT DELIVER EXACT TIME-DEPENDENT OR EXCITED STATES,

THE EXACT KOHN-SHAM THEORY WOULD DESCRIBE THE GROUND STATES OF ALL MATERIALS, WHETHER SIMPLE OR COMPLEX.

EXACT EXPRESSIONS ARE KNOWN FOR THE DENSITY FUNCTIONAL FOR THE EXCHANGE-CORRELATION ENERGY, BUT THEIR EVALUATION IS IMPRACTICAL. IN PRACTICE, THIS FUNCTIONAL MUST BE APPROXIMATED.

THE CHALLENGE OF COMPLEX MATERIALS IS TO MAKE THE APPROXIMATION ACCURATE ENOUGH AND RELIABLE ENOUGH TO CAPTURE THE SMALL ENERGY DIFFERENCES BETWEEN COMPETING STATES OR PHASES. MODEL HAMILTONIANS WITH FITTED PARAMETERS, WHICH ARE POPULAR FOR COMPLEX SYSTEMS IN PHYSICS, ARE USEFUL, BUT NEITHER GENERAL ENOUGH NOR MATERIALS-SPECIFIC ENOUGH FOR MATERIALS DISCOVERY.

TWO DIFFERENT WAYS TO CONSTRUCT DENSITY FUNCTIONAL APPROXIMATIONS:

(1) FIT TO A DATA-SET OF BONDED SYSTEMS (TYPICALLY ALSO SATISFYING A FEW EXACT CONSTRAINTS AND APPROPRIATE NORMS).

THIS APPROACH IS MORE "INTERPOLATIVE".

(2) SATISFY MANY EXACT CONSTRAINTS (KNOWN MATHEMATICAL PROPERTIES OF THE EXACT DENSITY FUNCTIONAL: EQUALITIES, BOUNDS, SCALING RELATIONS, LIMITS) AND APPROPRIATE NORMS (NON-BONDED SYSTEMS FOR WHICH THE APPROXIMATION CAN BE ACCURATE).

THIS "FIRST-PRINCIPLES" APPROACH IS MORE "PREDICTIVE". HOW ACCURATELY CAN IT PREDICT OVER THE IMMENSE SPACE OF POSSIBLE BONDED MATERIALS?

SOME COMPUTATIONALLY-EFFICIENT SEMI-LOCAL DENSITY FUNCTIONAL APPROXIMATIONS CONSTRUCTED BY APPROACH (2):

LOCAL SPIN DENSITY APPROXIMATION, 1965-1992

FITTED TO THE UNIFORM-DENSITY APPROPRIATE NORM, AND INHERITS SATISFACTION OF SEVERAL EXACT CONSTRAINTS THEREFROM

PERDEW-BURKE-ENZERHOF PBE GGA, 1996

SATISFIES 11 EXACT CONSTRAINTS AND THE UNIFORM-DENSITY APPROPRIATE NORM.

SCAN, THE STRONGLY CONSTRAINED AND APPROPRIATELY-NORMED META-GGA, SUN, RUZSINSZKY AND PERDEW 2015 (SUN)

SATISFIES ALL 17 EXACT CONSTRAINTS THAT A META-GGA CAN SATISFY. ITS APPROPRIATE NORMS INCLUDE THE UNIFORM DENSITIES AND SELECTED ATOMS.

SOME SUCCESSES OR FAILURES OF SCAN:

MUCH BETTER THAN PREVIOUS SEMI-LOCAL FUNCTIONALS FOR:

WATER AND WATER AT INTERFACES (WU, KLEIN, PERDEW)

FORMATION ENERGIES AND GROUND-STATE CRYSTAL STRUCTURES OF STRONGLY-BOUND SOLIDS (PENG, SUN, CEDER, PERDEW)

CRITICAL PRESSURES FOR STRUCTURAL PHASE TRANSITIONS OF SEMICONDUCTORS (SHAHI, PERDEW)

SOME "STRONGLY-CORRELATED" MATERIALS INCLUDING MnO2 AND THE CUPRATE HIGH-TEMPERATURE SUPERCONDUCTORS (GAP CLOSING UNDER DOPING, SPIN MOMENT ON CU ATOM, STRIPES AND STRIPE FLUCTUATIONS) (BANSIL, SUN, PERDEW)

GEOMETRIC AND MECHANICAL PROPERTIES OF MATERIALS, INCLUDING 2D MATERIALS (YAN, RUZSINSZKY)

SCAN HAS BEEN TESTED ON GRIMME's LARGE GMTKN55 SUITE OF 55 MOLECULAR DATA SETS. SCAN WAS THE BEST META-GGA TESTED, BUT WAS OUTPERFORMED BY SOME HYBRID FUNCTIONALS.

BUT, ON THE "MINDLESS BENCHMARKING SET" OF ARTIFICIAL MOLECULES NOT INCLUDED IN MOST FITTING SETS, SCAN OUTPERFORMED ALL OTHER FUNCTIONALS TESTED, INCLUDING HYBRIDS. THIS SHOWS THE PREDICTIVE POWER OF THE EXACT CONSTRAINTS.

SOMEWHAT BETTER THAN PREVIOUS SEMI-LOCAL FUNCTIONALS FOR:

MOST TRANSITION METAL OXIDES (WHERE SCAN NEEDS A SMALLER +U OR SELF-INTERACTION CORRECTION) (CARTER)

SOMEWHAT WORSE THAN PREVIOUS SEMI-LOCAL FUNCTIONALS (E.G., PBE) FOR:

FORMATION ENERGIES, MAGNETIC PROPERTIES, AND VACANCY ENERGIES IN TRANSITION METALS LIKE Fe OR V (ISSACS & WOLVERTON, SINGH)

EXTRA DEMANDS ON THE MESH FOR INTEGRATION OVER REAL SPACE (FURNESS, SUN)

NOT AS COMPATIBLE WITH EXISTING LONG-RANGE VAN DER WAALS CORRECTIONS (SZALEWICZ)

SCAN INTERPOLATES BETWEEN AND EXTRAPOLATES FROM KNOWN ISO-ORBITAL (1- OR 2-ELECTRON) AND SLOWLY-VARYING-DENSITY LIMITS, USING A DIMENSIONLESS VARIABLE α. WE ARE TRYING TO IMPROVE THE ACCURACY OF SCAN FOR THE TRANSITION METALS, AND TO REDUCE THE DEMANDS THAT SCAN MAKES ON THE REAL-SPACE MESH, BY SWITCHING TO THE DIMENSIONLESS VARIABLE β OF FURNESS AND SUN 2019.

J. FURNESS, A. KAPLAN, J. SUN, AND J.P. PERDEW (IN PROGRESS).

WE ARE ALSO TRYING TO DEVELOP A NONEMPIRICAL SELF-INTERACTION CORRECTION TO SCAN (OR MORE PRECISELY TO THE SCAN EXCHANGE ENERGY).

B. SANTRA, J.P. PERDEW, ET AL. (IN PROGRESS) (SANTRA, YANG)

WHAT HAVE WE LEARNED FROM THE PBE GGA AND SCAN META-GGA?

(1) THE PBE 1996 GGA IS THE MOST WIDELY-USED DENSITY FUNCTIONAL IN MATERIALS SCIENCE. AS A GGA, IT CONSTRUCTS THE XC ENERGY DENSITY FROM THE LOCAL SPIN DENSITIES AND THEIR GRADIENTS. IT SATISFIES 11 EXACT CONSTRAINTS AND THE UNIFORM-GAS APPROPRIATE NORM. IT IS NOT FITTED TO ANY BONDED SYSTEM. BUT IT HAS TO MAKE A CHOICE BETWEEN TWO CONSTRAINTS. IT IS MORE ACCURATE THAN THE LOCAL SPIN DENSITY APPROXIMATION, BUT NOT HIGHLY ACCURATE. HOWEVER, ITS ERRORS ARE USUALLY SYSTEMATIC.

(2) THE SCAN 2015 META-GGA IS USUALLY MORE ACCURATE THAN THE PBE GGA, FOR A MODEST (~FACTOR OF 3) INCREASE IN COMPUTATIONAL COST. AS A META-GGA, IT CONSTRUCTS THE XC ENERGY DENSITY FROM THE LOCAL DPIN DENSITIES, THEIR GRADIENTS, AND THE LOCAL ORBITAL KINETIC ENERGY DENSITY OF EACH SPIN. IT SATISFIES ALL 17 EXACT CONSTRAINTS THAT A META-GGA CAN SATISFY. IT SATISFIES THE UNIFORM-GAS APPRROPRIATE NORM, BUT REQUIRES ADDITIONAL APPROPRIATE NORMS SUCH AS ATOMS.

WITHOUT BEING FITTED TO ANY BONDED SYSYEM, SCAN DESCRIBES DIVERSE BONDS: COVALENT, METALLIC, HYDROGEN, AND INTERMEDIATE-RANGE VAN DER WAALS.

WHILE FUNCTIONALS FITTED TO MANY MOLECULES, WITH FEW EXACT CONSTRAINTS, TEND TO BE MORE "INTERPOLATIVE", SCAN TENDS TO BE MORE "PREDICTIVE".